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COMMENTS

Comment on the Electronic Reorganization in 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene

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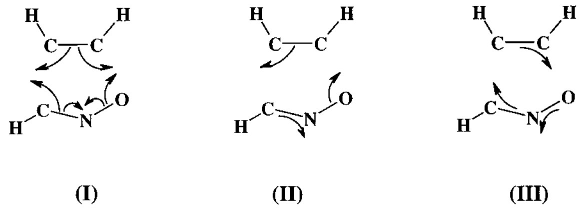
In this note, we comment on the electronic mechanism of the concerted 1,3-dipolar cycloaddition reaction of fulminic acid to acetylene (HCNO + HCCH), which has recently been studied by valence bond and molecular orbital approaches by four different groups including ourselves: (i) Sakata, K. *J. Phys. Chem. A* **2000**, *104*, 10001, (ii) Harcourt, R. D.; Schulz, A. *J. Phys. Chem. A* **2000**, *104*, 6510, (iii) Nguyen, M. T.; Chandra, A. K.; Sakai, S.; Morokuma, K. *J. Org. Chem.* **1999**, *64*, 65, and (iv) Karadakov, P. B.; Cooper, D. L.; Gerratt, J. *Theor. Chem. Acc.* **1998,** *100*, 222. The main discrepancy arising from these theoretical studies concerns the electronic reorganization, and in particular, the direction of the electron flow accompanying the nuclear deformation at the transition structure. We present additional results supporting our earlier findings that in the 1,3-dipolar cycloaddition of fulminic acid (HCNO) and probably substituted nitrile-oxides (RCNO), to alkynes and phosphaalkynes, the oxygen (O) atom behaves as a bond acceptor center and the carbon (C) as a bond donor.

The 1,3-dipolar cycloaddition is a general and powerful method for the synthesis of five-membered heterocyclic compounds owing to the great variety and availability of dipoles and dipolarophiles.[1] Therefore, the molecular mechanism of this pericyclic reaction has been the subject of numerous theoretical studies.[2,3] In particular, the electronic reorganization along the addition pathways has attracted considerable attention, not only as a textbook example for the migration of electron pairs[4] but also as an interpretive tool for the regioselectivity and substituents effect.[2]

Recently, four (4) theoretical studies[5−8] using different quantum chemical methods appeared dealing with the reaction between fulminic acid and acetylene (HCNO + HCCH), a prototypical 1,3-dipolar cycloaddition. The reported results disagreed with each other as to its electronic mechanism and in particular to the direction of the electron migration.

In their 1998 work, Karadakov, Cooper, and Gerratt (KCG)[5] used a valence bond (VB) approach in its modern spin-coupled form to follow the changes of valence orbitals of the HCNO + HCCH supersystem along the intrinsic reaction coordinate (IRC) pathway. These authors expressed their surprise to see that this reaction does not follow at all the usual spin-coupled pattern of a bond breaking/bond forming process as described in scheme I, in clear contrast to the case of the Diels−Alder cycloaddition also studied by them.[9] The concerted addition HCNO + HCCH was found to follow instead a heterolytic route, during which three orbital pairs corresponding to three distinct bonds of the reactants (the in-plane C−C, C−N, and N−O bonds) shift simultaneously to create the two new bonds closing the ring and a nitrogen lone pair. The process is thus achieved through movement of these pairs through space in which the orbitals become completely detached from their initial atomic center and end up localized about another center. Such an orbital relocation is illustrated in scheme II, in which the *oxygen center of fulminic acid was assigned as a new bond donor and the carbon as a new bond acceptor.* In simpler words, these authors[5] rejected the half-arrow mechanism (I) and supported the full-arrow one (II).



As a matter of fact, mechanism II was proposed long before by Leroy and co-workers[2,4] on the basis of the evolution of Boys localized orbitals (LMO) along the minimum energy path and is also in line with that found in the nucleophilic addition of water to fulminic acid.[10] The merit of these earlier studies[2,4] is that the essential features of the molecular mechanism could already be unraveled even using low-level Hartree−Fock wave functions with small basis sets and minimal and split-valence quality, available in the seventies for systems of this size.

In our 1999 study, Nguyen, Chandra, Sakai, and Morokuma (NCSM)[6] also analyzed the electron reorganization along the reaction path making use of two different approaches, namely, the configuration interaction−localized molecular orbitals−complete active space (CI−LMO−CAS) analysis[11] and the density functional theory-based reactivity descriptors[12] such as the Fukui function and local softness. Our CI−LMO analysis indicated that the addition starts with an electron migration from oxygen to nitrogen of the HCNO moiety, which finally makes *carbon a new bond donor center and oxygen a new bond acceptor center*, despite the fact that oxygen is the most negatively charged of the two centers. Such an electronic movement is also consistent with that derived from the reactivity descriptors that suggested that in HCNO, carbon bears a larger $\mathbf{f}^-$ value than oxygen (Fukui functions for electrophilic attack being an indicator for the electron donation ability). This electronic reshuffling is illustrated in scheme III, whose direction of the electron flow is clearly opposite to that shown in (II).

In a subsequent paper, Harcourt and Schulz (HS)[7] reported an analysis of the electronic structure of nitrous oxide (N_2O)

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and fulminic acid (HCNO) using a VB method and the minimal STO-6G basis set. Two main conclusions emerged from this theoretical study,[7] namely (i) in each of principal resonance structures found for the two 1,3-dipoles, the central nitrogen atom is apparently pentavalent, and (ii) a comparison of the different VB representations for the 1,3-dipolar cycloaddition of fulminic acid to acetylene led to the conclusion that the electronic reorganization that occurred during this reaction proceeds according to the more classical VB scheme I, which involves a homolytic breaking of the three π-bonds of the reactants and a recoupling of the spins associated with the orbitals describing these bonds to form new σ bonds of the adduct.

Regarding the first conclusion (i), we could easily agree with the authors bearing in mind that the apparent pentavalency of nitrogen represents specific resonance structures and the number of electrons actually located around the oxygen atom or between nitrogen and oxygen atoms is rather dependent on the theoretical method employed.[4] In contrast, the second conclusion (ii) causes much of our concern, as it differs fundamentally from those described in schemes II and III mentioned above. In any case, it seems that two different VB treatments led to two contrasting results.

While HS[7] have argued against the proposal (II), they have unfortunately not mentioned our relevant results and therefore not properly discussed the available propositions.

More recently, Sakata[8] reconsidered the electronic reorganization of the same reaction, making use of the derivatives of the atomic charges and bond orders derived from HF/6-31G(d,p) wave functions, with respect to nuclear motions along the IRC path, as well as a decomposition of the derivatives. The main result of this study[8] is another probe of the electronic character of the asynchronous bond formation in the [3+2] cycloaddition. The asynchronism of the bond formation was approached in earlier studies[2] by using energetic criteria. Mechanism II has been mentioned but not discussed. Moreover, both papers by NCSM[6] and HS[7] were overlooked.

In summary, three distinct viewpoints as given by (I), (II), and (III), on the electronic mechanism of the HCNO + HCCH reaction have been obtained by using three different types of wave functions. As it sometimes happened, very different results on a certain property could be obtained from different levels of electronic structure calculations. Nevertheless, in the present case, the diverging results were presented in a dispersed manner that a full account of them is not made yet. In this context, it seems to us desirable to take the opportunity offered by a Comment in this Journal to bring them together, to emphasize once more the remarkable difference of views all derived from quantum chemical treatments, on an issue of fundamental interest such as the electronic mechanism of a typical pericyclic reaction, and hopefully to stimulate some discussion and future studies. For our part, we wish to argue for the point that our proposal depicted in scheme III provides a better rationalization for the regioselectivity of these cycloadditions.

A way of differentiating these electronic mechanisms is in fact to examine the *regioselectivity* resulting from an addition of the dipole to either an asymmetrically substituted acetylene or a comparable hetero-dipolarophile. The existence of a polar partner with better-defined reaction sites leads to two regioisomers of the cycloadducts, and the kinetic preference of the one over the other could allow the reactive sites of the dipole to be identified. For this purpose, let us consider phosphaalkynes (RC≡P, with R = H, CH_3, CN) and monosubstituted acetylenes (RC≡CH, with R = H, CH_3, CN) as dipolarophiles.

In general, addition of a 1,3-dipole to a polar dipolarophile can be characterized by two transition structures. We can define a *normal addition* through a **TSn** and a *reverse addition* via a **TSr**: in a **TSn**, the migrating electron pairs in the partners move in a harmonious and complementary manner and in the same direction in such a way that a new bond is formed linking the dipole bond donor center with the dipolarophile bond acceptor center. Similarly, the second new bond is expected to connect the dipole bond acceptor center to the dipolarophile bond donor center. An opposite situation occurs in a **TSr**, which is expected to lie somewhat higher in energy than its **TSn** counterpart.

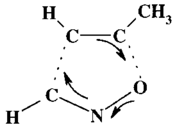
TSn **TSr**

(a) Addition H−C≡N=O + R−C≡P. Although phosphorus is isovalent with nitrogen, phosphaalkynes RCP present a reserve polarity as compared with cyanides RCN due to a small difference in electronegativities of C and P in favor of C. As a result, the reactivity of RCP is closer to that of alkynes than that of cyanides, and phosphorus usually behaves in RCP as a bond acceptor center. Previous B3LYP/6-31G(d,p) calculations[12] on both HCNO + RCP additions, with R = H and CH_3, showed that the normal addition as defined above is consistently favored over the reverse one. In the unsubstituted HCP, the energy barriers amount to 28 and 32 kJ/mol via **TSn/RCP** and **TSr/RCP**, respectively (values including zero-point energies). In the methylated dipolarophile CH_3CP, even though the barrier is actually increased, the normal addition having an energy barrier of 35 kJ/mol is strongly reinforced with respect to the reverse one (50 kJ/mol). In contrast, the cyano group in NCCP tends to reduce slightly the barriers, namely, 26 kJ/mol for the normal addition and 30 kJ/mol for the reverse. Such an effect of substituents could be anticipated, as electron donor groups on dipolarophiles usually slow the addition whereas withdrawing groups tend to accelerate it.[2]

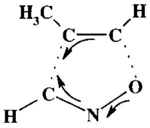
TSn/RCP **TSr/RCP**

The regioselectivity identified in such a way is consistent with numerous experimental results on cycloadditions of nitrile-oxides to phosphaalkynes, where 1,2,4-oxazaphospholes have been generated as the sole or major adduct[13] (cycles formed from **TSn/RCP**). Such a regioselectivity does not follow the chemical intuition based solely on the charge distribution but could now be understood in terms of the direction of the electron flow depicted in mechanism III.

(b) Addition H−C≡N=O + R−C≡CH. A monosubstitution of H in acetylene by electron donor groups as methyl and amino creates a slightly polar dipolarophile in which the substituted carbon atom (RC−) would be a bond donor center. In this sense, the RCCH moiety is expected to behave similarly to phosphaalkynes. Of the two transition structures **TSn/RCCH** and **TSr/RCCH**, the former is calculated to be invariably lower in energy than the latter. With respect to HCNO + CH_3CCH, the energy barriers obtained by B3LYP/6-31G(d,p)+ZPE calculations are 61 and 71 kJ/mol for the normal and reverse additions, respectively. Again, the methyl group slightly increases the energy barrier, which is calculated to be 56 kJ/mol in the parent HCNO + HCCH case at the same level of theory. In his study on the charge evolution along the IRC path, Sakata[8] found that the atomic charge on the acetylene carbon bonded to the HCNO oxygen decreases whereas the charge on the acetylene carbon attached to the HCNO carbon increases in the initial stage of the addition. We feel that this fact is a support for the view that in HCNO, the O-atom is a bond acceptor and the C-atom a bond donor. Nevertheless, we could not make any direct correlation between structure III and the changes in atomic charges.



TSn/RCCH



TSr/RCCH

Regarding the reaction involving cyano-acetylene, NCCCH, the same regiochemistry holds even though the difference in energy barriers for both normal and reverse approaches is reduced to 3 kJ/mol. With respect to the parent system, the cyano group also reduces the energy barrier by 5 kJ/mol.

Although we could expand the applications to a larger set of dipolarophiles, it seems that the above examples are compelling enough to point out that, of the three available propositions (I), (II), and (III) for the electronic mechanism of the 1,3-dipolar cycloaddition of HCNO, mechanism III recently suggested by us (NCSM)[6] considering the carbon of HCNO as a new bond donor center provides us with a consistent interpretation of the regioselectivity of its additions to either alkynes or phosphaalkynes.

It should be stressed that the structure (III) shows only the direction of electron flow in the initial stages of the 13DP cycloaddition reaction. The effective barrier height of a reaction also depends on the net amount of charge transfer between the two reactants. The net amount of charge transfer is somehow proportional to the chemical potentials difference between the reactants. The chemical potentials of HCNO, HCP, H_3C-CP, and NC−CP at the B3LYP/6-311G(d,p) level amount to -3.80, -4.93, -4.38, and -5.84 eV, respectively. Thus a charge-transfer stabilization should reach its largest value for HCNO + NC−CP, which has also the lowest barrier height for 13DP. A similar trend can also be observed for HCNO + R−CCH (R = H, CH_3, CN) reactions.

While we would anticipate that mechanism III is likely to hold for reactions of a large majority of substituted nitrile-oxides RCNO, we could not rule out the fact that mechanism II could become operative in reactions involving other types of (more) polar dipolarophiles. It is well-known that a small change in the frontier orbital energies of the partners could already induce a change in the nature of their dominant (or favorable) interactions and thereby the corresponding electronic mechanism. Further studies using modern quantum chemical methods and concepts beyond the frontier orbitals are certainly needed to rationalize this large domain of theoretically challenging and experimentally important pericyclic reactions.

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References and Notes

(1) Huisgen, R., *Angew. Chem., Int. Ed. Engl.* **1963**, *2,* 565 and 633.

(2) (a) Leroy, G.; Sana, M.; Burke, L. A.; Nguyen, M. T. In *Quantum Theory of Chemical Reactions*; Daudel, R., et al., Eds.; D. Reidel: Dordrecht, The Netherlands, 1979; Vol 1, p. 91. (b) Sana, M.; Leroy, G.; Dive, G.; Nguyen, M. T. *J. Mol. Struct. (THEOCHEM)* **1982**, *89,* 147.

(3) Houk, K. N.; Yamaguchi, K. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984.

(4) Daudel, R.; Leroy, G.; Peeters, D.; Sana, M. *Quantum Chemistry*; Wiley: New York, 1983.

(5) Karadakov, P. B.; Cooper, D. L.; Gerratt, J. *Theor. Chem. Acc.* **1998**, *100*, 222,

(6) Nguyen, M. T.; Chandra, A. K.; Sakai, S., Morokuma, K. *J. Org. Chem.***1999**, *64*, 65.

(7) Harcourt, R. D.; Schulz, A. *J. Phys. Chem. A* **2000**, *104*, 6510.

(8) Sakata, K. *J. Phys. Chem. A* **2000**, *104*, 10001.

(9) Karadakov, P. B.; Cooper, D. L.; Gerratt, J. *J. Am. Chem. Soc.* **1998**, *120*, 3975.

(10) Nguyen, M. T., Sana, M.; Leroy, G.; Dignam, K. J.; Hegarty, A. F. *J. Am. Chem. Soc.* **1980**, *102*, 573.

(11) Sakai, S. *J. Phys. Chem. A* **1997**, *101*, 1140.

(12) Chandra, A. K.; Nguyen, M. T. *J. Phys. Chem. A* **1998**, *102*, 6181; *J. Comput. Chem.* **1998**, *19*, 195; *J. Chem. Soc., Perkin Trans. 2* **1997**, 1415.

(13) Regitz, M. *Chem. Rev.,* **1990,** *90*, 191.